# On Surface Ordering in Solutions of Rigid Rodlike Molecules(Session III : Complex Fluids, The 1st Tohwa University International Meeting on Statistical Physics Theories, Experiments and Computer Simulations)

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# On Surface Ordering in Solutions of Rigid Rodlike Molecules

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Simple model is developped to describe the surface ordering and the adsorption phenomena in solutions of rigid rodlike molecules. The surface properties of rigid rodlike molecules plays an important role to many practical processes, especially in display devices. In this reasen an understanding of their behavior near surface is of crucial significance. It is well known that solutions of rigid rodlike molecules show a transition from an isotropic to a nematic state and the transition is of the first order. This behavior is induced by the excluded volume interaction, or concentration. When the rods are adsorbed to the surfece from a bulk solution, the surface phase may also show a ordered state depending on the adsorption amounts, or the surface concentration. The adsorption energy considered here is of the order of thermal energy, so that we can expect surface ordering behavior when the surface concentration is increased.

From a simple discussion, we see that the surface of solutions of rigid rodlike molecules has some phase transitions. We here consider the attractive wall which corresponds to preferential adsorption of rodlike molecules. At extremely dilute solutions, both the bulk and the surface phases are in isotropic states. When the bulk concentration $\phi$ increases, the surface phase changes from an isotropic to a nematic state at a bulk concentration $\phi_c$. With a further increase of the bulk concentration, the isotropic-nematic transition (INT) in the bulk phase takes place at a bulk concentration $\phi_{IN}$. We then can expect the wetting of an isotropic bulk phase by a nematic surface for the range of concentrarion $\phi_c < \phi < \phi_{IN}$. For more concentrated solution $\phi > \phi_{IN}$, we can expect the wetting of a nematic bulk phase by a more ordered nematic surface phase.

In this paper we present a simple model to describe the surface ordering and the adsorption in solutions of rigid rodlike molecules. Here we focus on the planar adsorption of the rods to a surface. In general, an adsorbed rods may take an infinite number of orientations to the surface [1]. We here assume for simplicity that the possible orientations of the rods in the surface(bulk) phase are restricted to two(three) mutually orthogonal deirections. On the basis of the DiMarzio lattice model[2] with restricted rod orientations, we examine the molecular orientations in both bulk and the surface phases and we calculate the adsorption amounts, the surface tension, and the surface ordering behavior as a function of the adsorption energy, the axial-ratio of the rods, and the bulk concentration. The rigid rodlike molecules adsorbed to a surface cannot exhibit the INT in the bulk phase because of there is no translational degree of freedom normal to the surface. In our model, a second-order INT occures in the surface phase.

In Figure 1, the surface order parameters $s$ and the bulk order parameter $t$ are shown against the bulk volume fraction. The nematic(isotropic) phase corresponds to the region $s > 0$ or $t > 0 (s = 0$ or $t = 0)$. The surface order parameter is continuousry increased from $\phi_c$, where the INT takes place in the surface phase and the order parameter of a bulk phase, however, jumps at $\phi_{IN}$, where the INT occures in the bulk phase. For the range of concentrarion $\phi_c < \phi < \phi_{IN}$, we predict the wetting of an isotropic bulk phase by a nematic surface phase. For the concentrated solution $\phi > \phi_{IN}$, the more ordered nematic surface phase wets the nematic bulk phase.

Figure 2 shows the adsorption amounts $\phi_s$ plotted against the bulk volume fraction $\phi$ for the axia ratio $x = 10$. The adsorption isotherms has a kink at the bulk concentration $\phi_c$. Further increasing concentration, the adsorption amount is increased and the desorption occures at th bulk concentration $\phi_{IN}$, where two phases of the different surface concentration can coexist on the surface phase.

In conclusion, there are some types of wetting properties in solutions of rigid rodlike molecules and the effects of surface ordering are also appeared in adsorption isotherms.

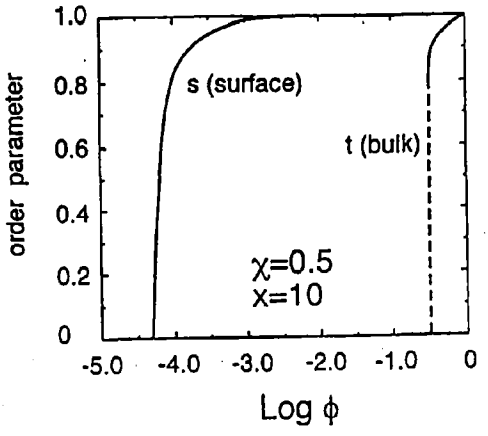


Figure 1. Surface order parameters $s$ and bulk order parameter $t$ are shown against the bulk volume fraction for the axia ratio $x = 10$. The isotropic-nematic transition in the bulk phase is indicated by a dotted line. The surface order parameter is continuousry increased with increasing concentration.

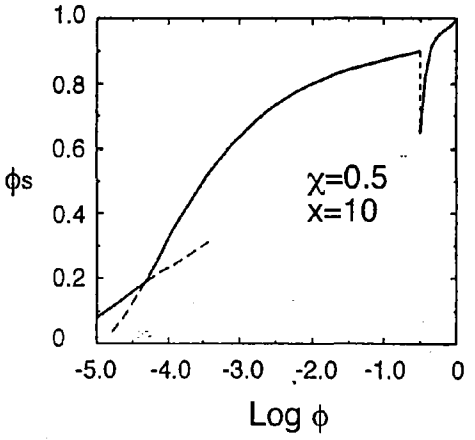


Figure 2. Adsorption isotherm plotted against the bulk volume fraction $\phi$ for the axial ratio $x = 10$.

References

(1) A. Matsuyama and T. Katoh, Macromolecules, **28**, 131 (1995).

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